



PCT/AU98/00854

9/529495

REC'D 06 NOV 1998

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I, KIM MARSHALL, MANAGER EXAMINATION SUPPORT AND SALES,
hereby certify that the annexed is a true copy of the Provisional specification in
connection with Application No. PO 9767 for a patent by ICI AUSTRALIA
OPERATIONS PTY LTD filed on 14 October 1997.

I further certify that the annexed specification is not, as yet, open to public
inspection.



WITNESS my hand this Twenty-third
day of October 1998

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ICI Australia Operations Pty Ltd

A U S T R A L I A

Patents Act 1990

PROVISIONAL SPECIFICATION

for the invention entitled:

"Method and Composition (III)"

The invention is described in the following statement:

METHOD AND COMPOSITION (III)

The present invention relates generally to dispersants, for use in agricultural applications, in particular the present invention relates to methods for the dispersion of insoluble material with copolymeric dispersants which dispersions are formed with improved dispersibility and show improved suspensibility. The present invention also relates to methods of producing dispersible formulations, the formulations per se and methods of treating substrates with dispersions produced from such formulations.

10 The active principles in many agricultural applications are largely hydrophobic or water insoluble in character and are, by necessity, often administered as finely divided solids suspended in aqueous media. The majority of these active principles are manufactured and marketed in concentrated form, possibly with the addition of other insoluble inert fillers, which are then diluted prior to application. For example, the active principle is typically available in the form of a suspension concentrate (SC), wettable powder (WP) or water dispersible granule (WG). However, due to the generally hydrophobic nature of the active principle, the addition of a suitable dispersant is essential in order to achieve an homogenous dispersion with a minimum of mixing, such as may be achieved readily by hand or with minimal mechanical mixing. Furthermore, once an homogenous dispersion is achieved, the resulting suspension must remain stable for a time sufficient, at least, to allow application by usual means such as spraying. Any settling, agglomeration or flocculation of the finely divided solid may lead to inconsistent and ineffective application as well as blockage of the

spraying equipment. It is therefore necessary to provide a dispersant which provides easy and
~~homogenous dispersion and results in a suspension which maintains its stability during the~~
application of the aqueous dispersion.

5 Effective dispersants for use in these applications ideally provide a suspension with acceptable dispersibility, suspensibility and lack of agglomeration. The Collaborative International Pesticides Analytical Council (CIPAC Handbook Volume 1) defines methods that can be used for determining acceptable suspensibility (MT 15.1) and degree of agglomeration (MT 59.3). For example, in suspension concentrates so-called SC
10 formulations, this can be achieved by the addition of about 3-5 w/w% of a standard dispersant. Wettable powder (WP) and water dispersible granule (WG) formulations generally require the addition of standard dispersant in the order of 6-7 w/w% in order to achieve acceptable suspensibility and degree of agglomeration as determined by a wet sieve retention test. (MT 59.3).

15

Currently used dispersants for SC formulations include ethylene oxide/propylene oxide block copolymer surfactants based on an hydrophobic moiety plus ethyleneoxide. Also used are ether phosphate derivatives of non-ionic surfactants, especially of tristyrylphenol ethoxylates. Conventional anionic surfactants used include sulphonated derivatives of arylformaldehyde
20 condensates, polyacrylates and lignosulfonates.

Dispersants for WP and WG formulations are usually limited by the requirement that the

dispersant be solid at ambient temperatures, be non-gelling and not dissolve the active

~~principle. For these reasons, conventional non-ionic surfactants are often unsuitable, and~~

anionic dispersants are preferred. Known effective dispersants for WP and WG formulations include sulphonated alkyl naphthalene/formaldehyde condensate salts and lignosulfonate salts.

5

α -Olefin-polycarboxylate copolymers are well known as dispersants in a wide range of applications including pigment dispersion, emulsion polymerisation, cosmetics and pesticidal compositions. As far back as 1972 the sodium salt of a maleic anhydride and diisobutylene copolymer was given an exemption from tolerance for use in pesticide formulations by the

10 United States Environmental Protection Authority following a petition from Rohm and Haas Co. FR 2545325 describes the use of ammonium and alkali metal salts of maleic anhydride-diisobutylene copolymer in pesticide granules. Similarly, EP 201417 describes the use of copolymers of maleic anhydride with surfactants selected from sulfates and phosphates of ethoxylated phenol derivatives in WP and WG formulations. JP 62036302 describes

15 copolymers having a molecular weight range of from 5000-20000 for use with granular agrochemical compositions. Maleic anhydride and diisobutylene copolymer derivatives are described for use in conjunction with CaCO_3 and Mg salts for SC formulations in JP 06 09,302. The use of sulfonated derivatives of copolymers of maleic anhydride in water dispersable granules is also described in JP 58-131903.

20

French Patent No. 2,397,444 describes stable and concentrated dispersions of active materials may be prepared from non-dusting powders or granular materials. It is necessary to separate

the active material in the presence of a salt of an acidic resin, such as, for example, a
~~copolymer of maleic anhydride and an α -olefinic compound; add an organic solvent which~~
forms, together with the aqueous medium, a two-phase system; treat such two-phase system
by adding a carrier substance thereto; and then isolate the product by a reduction in the
5 volume of the organic phase by the addition of water, the solvent gradually transferring into
the added water.

We have now found in a first embodiment of the present invention that the use of a range of
derivatisations of alternating copolymers of an α,β -unsaturated oxyacid and an olefin having
10 one or more polymerizable double bonds provides improved dispersibility and suspensibility
in agrochemical formulations, compared to those dispersants already described in the prior
art, as well as a number of other ancillary benefits which will be more fully described herein.

We have also found in a second embodiment that the use of certain of the range
15 derivatisations surprisingly provides improvements in dispersibility and suspensibility not only
in alternating copolymers but in a range of other copolymers including random and block
copolymers.

According to a first aspect of the present invention, there is provided a method of dispersing
20 an insoluble material in an aqueous solution comprising the following steps:

- (i) providing a formulation comprising at least one insoluble material and at least one

dispersant comprising an agriculturally acceptable salt or water soluble agriculturally

~~acceptable derivative of an alternating copolymer wherein said alternating copolymer~~

comprises a residue of a first comonomer and a residue of a second comonomer,

wherein said first comonomer comprises α,β -unsaturated oxyacids or anhydrides and

5 said second comonomer comprises olefinic compounds containing one or more polymerizable double bonds; and

(ii) dispersing said formulation in an aqueous medium.

10 According to a second aspect of the present invention, there is provided a method of making an agrochemical formulation comprising the steps of:

(i) combining at least one insoluble material, and at least one dispersant comprising an agriculturally acceptable salt or water-soluble agriculturally acceptable derivative of
15 an alternating copolymer wherein said alternating copolymer comprises a residue of a first comonomer and a residue of a second comonomer, wherein said first comonomer comprises α,β -unsaturated oxyacids or anhydrides and said second comonomer comprises olefinic compounds containing one or more polymerizable double bonds;

20

(ii) milling said combination to a particle size range in order to obtain a stable, readily-suspendible aqueous dispersion; and

- (iii) stabilising said aqueous dispersion to obtain an SC formulation suitable for dilution
in water for agricultural use.

According to a third aspect of the present invention, there is provided a method of making
5 an agrochemical formulation comprising the steps of:

- (i) combining at least one insoluble material, with at least one dispersant comprising an
agriculturally acceptable salt or water-soluble agriculturally acceptable derivative of
an alternating copolymer wherein said alternating copolymer comprises a residue of
10 a first comonomer and a residue of a second comonomer, wherein said first
comonomer comprises α,β -unsaturated oxyacids or anhydrides and said second
comonomer comprises olefinic compounds containing one or more polymerizable
double bonds; and
- 15 (ii) milling said combination to a desired particle size to obtain a homogeneous wettable
powder (WP) formulation.

According to a fourth aspect of the present invention, there is provided a method of making
an agrochemical formulation comprising the steps of:

20

- (i) combining at least one insoluble material suitable for agricultural use with at least one
dispersant comprising an agriculturally acceptable salt or water-soluble agriculturally

acceptable derivative of an alternating copolymer wherein said alternating copolymer

~~comprises a residue of a first comonomer and a residue of a second comonomer,~~

wherein said first comonomer comprises α,β - unsaturated oxyacids or anhydrides and

said second comonomer comprises olefinic compounds containing one or more

5 polymerizable double bonds; and

(ii) blending said combination to obtain a homogeneous wettable powder (WP) formulation.

10 According to a fifth aspect of the present invention, there is provided a method of making an agrochemical formulation comprising the steps of:

(i) combining at least one insoluble material suitable for agricultural use with at least one dispersant comprising an agriculturally acceptable salt or water-soluble agriculturally acceptable derivative of an alternating copolymer wherein said alternating copolymer comprises a residue of a first comonomer and a residue of a second comonomer, wherein said first comonomer comprises α,β -unsaturated oxyacids or anhydrides and said second comonomer comprises olefinic compounds containing one or more polymerizable double bonds;

20

(ii) agglomerating said combination to form discrete granular materials; and

- (iii) drying said granular materials to obtain a water dispersible granule WG formulation.
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According to a sixth aspect of the present invention, there is provided a formulation produced by the process of the second, third, fourth and fifth aspects.

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According to a seventh aspect of the present invention, there is provided an agricultural formulation comprising at least one insoluble material and at least one dispersant comprising an agriculturally acceptable salt or water-soluble agriculturally acceptable derivative of an alternating copolymer wherein said alternating copolymer comprises a residue of a first
10 comonomer and a residue of a second comonomer, wherein said first comonomer comprises α,β -unsaturated oxyacids or anhydrides and said second comonomer comprises olefinic compounds containing one or more polymerizable double bonds.

According to an eighth aspect of the present invention, there is provided a method of
15 treatment of a substrate with a insoluble material comprising the following steps:

- (i) preparing a formulation comprising at least one insoluble material and at least one dispersant comprising an agriculturally acceptable salt or water-soluble agriculturally acceptable derivative of an alternating copolymer wherein said alternating copolymer
20 comprises a residue of a first comonomer and a residue of a second comonomer, wherein said first comonomer comprises α,β -unsaturated oxyacids or anhydrides and said second comonomer comprises olefinic compounds containing one or more

polymerizable double bonds;

- (ii) dispersing said formulation in an aqueous medium; and
- 5 (iii) applying the dispersed formulation to a substrate.

○ The dispersants for use in the first embodiment of the present invention are based on alternating copolymers. It will be understood by those skilled in the art that alternating copolymers may be prepared by the careful selection of comonomers and reaction conditions.

10 As is well known in the art, often additional polymerization conditions should be observed in order to obtain an alternating copolymer. For example the temperature and type of solvent can influence whether an alternating or other type of copolymer is formed. Methods for making such alternating copolymers will be well known to those skilled in the art of polymer synthesis.

○ 15

The alternating, or substantially alternating character, of the copolymers is believed to be critical to this first embodiment of the present invention. The person skilled in the art will understand the degree of regularity necessary in order for a copolymer to be considered of alternating character. It is preferred that the alternating copolymer has an alternating
20 character defined by greater than 70% of consecutive comonomer residue units being alternate between residues of the first comonomer and the second comonomer, more preferably greater than 90%. A high degree of control in the synthesis of such copolymers is required in most

cases to achieve this.

Alternating copolymers may be made by copolymerising (1) an unsaturated monomer, or mixture of monomers, having at least one reactive double bond wherein the balance of
5 substituents on the double bond make the double bond electron deficient compared to styrene, which is used by those proficient in the art of polymer chemistry as a benchmark monomer, (ref. Polymer Handbook, section II/267), together with (2) an unsaturated monomer having at least one double bond that is copolymerisable with monomer (1) wherein the balance of substituents on the double bond are such as to make it the double bond electron rich compared
10 to monomer (1).

Examples of suitable monomers of (1) include fumaric acid, maleic acid and anhydrides, and the esters, amides and imides derived from them, itaconic acid and anhydride and the corresponding esters amides and imides derived from them, acrylic and methacrylic acids,
15 esters and amides, vinylphosphonic acid and the corresponding esters and amides derived from it and ethylene sulphonic acid and the esters and amides derived from it.

Examples of suitable monomers of (2) include styrene and its alkyl and halo derivatives, vinyl ethers and esters, α -olefins, internal olefins, cyclic olefins, both exocyclic and endocyclic,
20 allylic alcohols and their corresponding ester derivatives, allylic ethers and allylic halo compounds, allylic aryl compounds, vinyl amides, vinyl chloride and vinylidene chloride.

While not wishing to be bound by theory it is believed that the imbalance of electron deficient and electron rich double bonds of monomers (1) and (2) confers a substantially alternating character to the copolymers derived therefrom as opposed to random or block homopolymerisation character. While not wishing to be bound by theory it appears that the alternating character of the copolymer derivatives provides either a consistent and regular charge density or a steric barrier to aid dispersant performance and also afford improved water solubility.

The dispersants of the first embodiment of the present invention incorporate agriculturally acceptable salts or water-soluble agriculturally acceptable derivatives of the alternating copolymer and are preferably readily soluble in water. Suitable agriculturally acceptable salt derivatives include those obtained by reacting groups pendant to the copolymer such as acids and acid derivatives, such as anhydrides and esters, with basic reagents such as alkali and alkaline earth metal hydroxides, oxides, carbonates and alkoxides, or basic nitrogen, sulphur and phosphorous compounds such as ammonia, amines and tetraalkylammonium, sulphonium and phosphonium salts. While agriculturally acceptable salts of the alternating copolymer are generally preferred, the free acid of the alternating copolymer may be provided in the formulation and a separate source of suitable cations which on addition to aqueous media solubilises the alternating copolymer. The free acid of the alternating copolymer is not generally soluble in water.

The formulation may contain the free acid of the alternating copolymer (in the absence of any

suitable cation source). A cation source may be provided in a separate addition to the aqueous medium prior to the dispersing of the formulation.

Cation sources suitable for incorporation into either the formulation or the aqueous medium include sources of agriculturally acceptable cations, such as alkali metal cations. Preferably the cation source is selected from the group consisting of alkaline salts such as carbonates, hydroxides, phosphates, alkoxides, borates, sulphites and silicates. Other water soluble agriculturally acceptable derivatives of the alternating copolymer include polyalkyleneoxy derivatives, polyamide derivatives and polyvinyl alcohol derivatives. By water-soluble it is meant that the derivatives of the alternating copolymer are at least partially water-soluble at ambient temperatures. Other water-soluble derivatives of the alternating copolymer are also useful in the present invention.

The alternating copolymer may contain additional comonomer residues. For example, the addition of a small amount, say less than 10%, of methyl methacrylate will not substantially change the alternating character of the copolymer. Suitable alternating copolymers for use in the present invention also include copolymers of three or more comonomers. While not wishing to be bound by theory it appears that providing a consistent hydrophobic polymer backbone is provided in the presence of regularly spaced anionic charge or steric barrier along the polymer molecule such as obtained by an alternating copolymer, the improved dispersant performance is preserved.

The preferred molecular weights of the alternating copolymers are in the range of from 1000

to 90000 daltons. We have found that certain higher molecular weight alternating copolymers show a certain degree of intractability in solution and our more preferred range is from 1000-30000 daltons, even more preferred is 1000-10000 daltons.

- 5 We have found that agriculturally acceptable salts or other water soluble derivatives of alternating copolymers for use as dispersants in agricultural compositions provide improved and consistent dispersant performance when compared to conventionally used dispersants such as sulphonated alkylnaphthalene formaldehyde condensate salts.
- 10 Methods for making such alternating copolymers will be well known to those skilled in the art of polymer synthesis.
- The dispersant system used in embodiments of the present invention may be a mixture of the alternating copolymer with other dispersants known to those skilled in the art, including alkyl
- 15 substituted and unsubstituted sulfonated naphthalene formaldehyde condensate salts, alkyl substituted and unsubstituted phenol formaldehyde condensate salts, lignosulphonate salts, polyacrylate salts, and other previously disclosed α -olefinic-unsaturated dicarboxylic acid copolymer derivatives.
- 20 In the second embodiment improved dispersibility and suspensibility has been found not only in certain selected alternating copolymers but surprisingly also in other copolymer derivatives including those of random and block copolymers.

According to a ninth aspect of the present invention, there is provided a method of dispersing
~~an insoluble material in an aqueous solution comprising the following steps:~~

- (i) providing a formulation comprising at least one insoluble material and at least one
5 dispersant comprising a copolymer wherein said copolymer comprises a residue of a
first comonomer and a residue of a second comonomer, wherein said first comonomer
is an α,β -unsaturated oxyacid or anhydride and said second comonomer is an olefin
having at least one polymerizable double bond and wherein at least one of said first
comonomer and said second comonomer is substituted, wherein the substituents for
10 said first comonomer are selected from the group consisting of esters, amides,
thioesters and functional groups derived from reaction with nucleophilic reagents and
wherein the substituents for the second comonomer are selected from the group
consisting of epoxides; sulfonates; esters; amides; and optionally substituted pendent
aromatic and heteroaromatic groups wherein said optional substituents are selected
15 from the group consisting of sulfonates, nitrates, phosphates and other substituents
derived from reaction with electrophilic reagents.
- (ii) dispersing said formulation in an aqueous medium.

20 According to a tenth aspect of the present invention, there is provided a method of making
an agrochemical formulation comprising the steps of:

- (i) combining at least one insoluble material, and at least one dispersant comprising a copolymer wherein said copolymer comprises a residue of a first comonomer and a residue of a second comonomer, wherein said first comonomer is an α,β -unsaturated oxyacid or anhydride and said second comonomer is an olefin having at least one polymerizable double bond and wherein at least one of said first comonomer and said second comonomer is substituted, wherein the substituents for said first comonomer are selected from the group consisting of esters, amides, thioesters and functional groups derived from reaction with nucleophilic reagents and wherein the substituents for the second comonomer are selected from the group consisting of epoxides; sulfonates; esters; amides; and optionally substituted pendent aromatic and heteroaromatic groups wherein said optional substituents are selected from the group consisting of sulfonates, nitrates, phosphates and other substituents derived from reaction with electrophilic reagents;
- 15 (ii) milling said combination to a particle size range in order to obtain a stable, readily-suspendible aqueous dispersion; and
- (iii) stabilising said aqueous dispersion to obtain an SC formulation suitable for dilution in water for agricultural use.

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According to a eleventh aspect of the present invention, there is provided a method of making an agrochemical formulation comprising the steps of:

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- (i) combining at least one insoluble material, with at least one dispersant comprising a copolymer wherein said copolymer comprises a residue of a first comonomer and a residue of a second comonomer, wherein said first comonomer is an α,β -unsaturated oxyacid or anhydride and said second comonomer is an olefin having at least one polymerizable double bond and wherein at least one of said first comonomer and said second comonomer is substituted, wherein the substituents for said first comonomer are selected from the group consisting of esters, amides, thioesters and functional groups derived from reaction with nucleophilic reagents and wherein the substituents for the second comonomer are selected from the group consisting of epoxides; sulfonates; esters; amides; and optionally substituted pendent aromatic and heteroaromatic groups wherein said optional substituents are selected from the group consisting of sulfonates, nitrates, phosphates and other substituents derived from reaction with electrophilic reagents; and
- 15 (ii) milling said combination to a desired particle size to obtain a homogeneous wettable powder (WP) formulation.

According to a twelfth aspect of the present invention, there is provided a method of making an agrochemical formulation comprising the steps of:

20

- (i) combining at least one insoluble material suitable for agricultural use with at least one dispersant comprising a copolymer wherein said copolymer comprises a residue of a

first comonomer and a residue of a second comonomer, wherein said first comonomer is an α,β -unsaturated oxyacid or anhydride and said second comonomer is an olefin

having at least one polymerizable double bond and wherein at least one of said first comonomer and said second comonomer is substituted, wherein the substituents for said first comonomer are selected from the group consisting of esters, amides, thioesters and functional groups derived from reaction with nucleophilic reagents and wherein the substituents for the second comonomer are selected from the group consisting of epoxides; sulfonates; esters; amides; and optionally substituted pendent aromatic and heteroaromatic groups wherein said optional substituents are selected from the group consisting of sulfonates, nitrates, phosphates and other substituents derived from reaction with electrophilic reagents; and

(ii) blending said combination to obtain a homogeneous wettable powder (WP) formulation.

According to a thirteenth aspect of the present invention, there is provided a method of making an agrochemical formulation comprising the steps of:

(i) combining at least one insoluble material suitable for agricultural use with at least one dispersant comprising a copolymer wherein said copolymer comprises a residue of a first comonomer and a residue of a second comonomer, wherein said first comonomer is an α,β -unsaturated oxyacid or anhydride and said second comonomer is an olefin

having at least one polymerizable double bond and wherein at least one of said first

~~comonomer and said second comonomer is substituted, wherein the substituents for~~

said first comonomer are selected from the group consisting of esters, amides, thioesters and functional groups derived from reaction with nucleophilic reagents and

5 wherein the substituents for the second comonomer are selected from the group consisting of epoxides; sulfonates; esters; amides; and optionally substituted pendent aromatic and heteroaromatic groups wherein said optional substituents are selected from the group consisting of sulfonates, nitrates, phosphates and other substituents derived from reaction with electrophilic reagents;

10

(ii) agglomerating said combination to form discrete granular materials; and

(iii) drying said granular materials to obtain a water dispersible granule WG formulation.

15 According to a fourteenth aspect of the present invention, there is provided a formulation produced by the process of the tenth, eleventh, twelfth and thirteenth aspects.

According to a fifteenth aspect of the present invention, there is provided an agricultural formulation comprising at least one insoluble material and at least one dispersant comprising

20 a copolymer wherein said copolymer comprises a residue of a first comonomer and a residue of a second comonomer, wherein said first comonomer is an α,β -unsaturated oxyacid or anhydride and said second comonomer is an olefin having at least one polymerizable double

- bond and wherein at least one of said first comonomer and said second comonomer is substituted, wherein the substituents for said first comonomer are selected from the group consisting of esters, amides, thioesters and functional groups derived from reaction with nucleophilic reagents and wherein the substituents for the second comonomer are selected from the group consisting of epoxides; sulfonates; esters; amides; and optionally substituted pendent aromatic and heteroaromatic groups wherein said optional substituents are selected from the group consisting of sulfonates, nitrates, phosphates and other substituents derived from reaction with electrophilic reagents.
- 10 According to an sixteenth aspect of the present invention, there is provided a method of treatment of a substrate with a insoluble material comprising the following steps:
- (i) preparing a formulation comprising at least one insoluble material and at least one dispersant comprising a copolymer wherein said copolymer comprises a residue of a first comonomer and a residue of a second comonomer, wherein said first comonomer is an α,β -unsaturated oxyacid or anhydride and said second comonomer is an olefin having at least one polymerizable double bond and wherein at least one of said first comonomer and said second comonomer is substituted, wherein the substituents for said first comonomer are selected from the group consisting of esters, amides, thioesters and functional groups derived from reaction with nucleophilic reagents and wherein the substituents for the second comonomer are selected from the group consisting of epoxides; sulfonates; esters; amides; and optionally substituted pendent

aromatic and heteroaromatic groups wherein said optional substituents are selected from the group consisting of sulfonates, nitrates, phosphates and other substituents derived from reaction with electrophilic reagents;

5 (ii) dispersing said formulation in an aqueous medium; and

(iii) applying the dispersed formulation to a substrate.

The derivitisation of the copolymer is of central importance to the second embodiment of the
10 invention herein described. While not wishing to be bound by theory, it appears that in addition to the enhanced solubility in water, it may confer additional polarity or charge density to the dispersant such as to enhance its performance. Further it may lead to better conformational alignment of the copolymer and therefore the copolymer is more readily soluble and may more readily align itself with surfaces. We have found that a non alternating
15 polymer which is unsuitable for use as a dispersant when used as an alkali metal or quaternary ammonium salt derivative is significantly improved in dispersant performance when derivatised according to the second embodiment of the present invention.

The first comonomer for use in the second embodiment of the present invention may be
20 substantially the same as the first comonomer for use in the first embodiment of the present invention.

The second comonomer for use in the second embodiment of the present invention is an olefin having at least one polymerizable double bond which may be substituted as defined herein.

The second comonomer for use in the second embodiment of the present invention may be an alicyclic monomer having a polymerizable exo-cyclic double bond. It will be understood that by alicyclic monomer is meant an aliphatic cyclic monomer containing moieties such as a cyclic alkyl, cyclic alkenyl or heterocyclic groups and which may comprise one or more carbocyclic or heterocyclic rings. It will be understood that by exo-cyclic is meant an alkylidene substituted cyclic structure. Alicyclic monomers having a polymerizable exo-cyclic double bond may optionally be substituted. Alicyclic monomers having a polymerizable exo-cyclic double bond of the present invention may include, for example, β -pinene, 5-ethylidene-2-norbornene, methylene cyclohexane and methylene cyclopentane. The most preferred alicyclic monomer having a polymerizable exo-cyclic double bond.

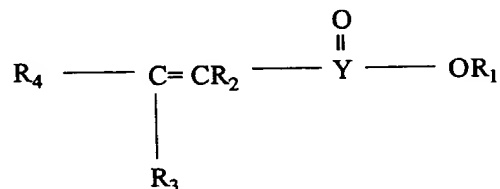
15 The second comonomer for use in the second embodiment of the present invention may be an alicyclic monomer having a polymerizable endo-cyclic double bond. The term alicyclic monomer is as hereinabove defined. It will be understood that by endo-cyclic is meant the polymerizable double bond has both ends (or termini) forming part of the cyclic structure of the alicyclic monomer. Alicyclic monomers having a polymerizable endo-cyclic double bond may optionally be substituted. Alicyclic monomers having a polymerizable endocyclic double bond may include substituted and unsubstituted norbornene, cyclopentadiene and substituted cyclopentadienes, substituted and unsubstituted dicyclopentadienes, cyclohexenes,

furans and indenenes. Most preferred of the above monomers containing an endo-cyclic double bond are dicyclopentadiene and dimethyldicyclopentadiene.

The second comonomer for use in the second embodiment of the present invention may be an α -olefin having at least one cyclic substituent. It will be understood that by α -olefin is meant an olefinic compound having a terminal double bond. Suitable cyclic substituents include benzene and substituted benzene, cyclopentane, cyclohexane, and other cycloaliphatics, heterocyclics, heteroaromatics, aromatics and polyaromatics. Examples of suitable α -olefinic cyclic compounds include limonene and similar terpenes, vinyl cyclohexanes, vinyl cyclohexenes, vinyl pyridines, vinyl thiophenes, vinyl naphthalenes, vinyl furans, vinyl pyrans and, vinyl pyrrolidones. Most preferred α -olefin cyclic monomers include d-limonene, vinyl naphthalene, vinyl pyrrolidone, allyl glycidyl ether and vinyl cyclohexene.

15 The second comonomer of the second embodiment of the present invention may be an α -olefin having an alkyl group such as diisobutylene, isobutylene, n-octene, n-decene, allylglycidylether or vinylisobutylether. The second comonomer may also be an internal olefin.

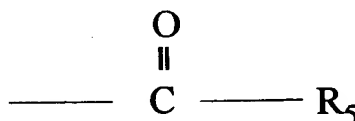
Preferred examples of the first comonomer may be described as having structure I



I

- 5 wherein R_1 is M a metal, quaternary ammonium, phosphonium or sulphonium residue, R_2 is hydrogen or C_1 to C_4 alkyl is a carbon atom, $\text{O}=\text{S}$, or POR a hydrogen atom or alkyl radical having from 1 to 10 carbon atoms (or carboxylated such radical) and R_4 is H, an alkyl radical or a carboxylic acid derivative of form II

10



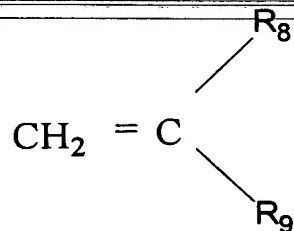
II

wherein R_5 is OR_6 , NR_6R_7 , SR_6 ,

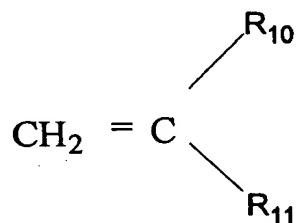
wherein R_6, R_7 , are H, alkyl, O-alkyl, or alkyl groups with a hetero atom substituent. The

- 15 second comonomer may be alternatively described as a residue having formula III

- 25 -

**III**

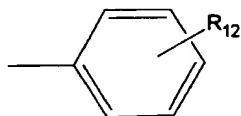
wherein R_8 represents hydrogen, a straight or branched chain alkyl of from 1-4 carbon atoms,
5 R_9 represents hydrogen, a branched chain alkyl radical from 1-12 carbon atoms, or cycloalkyl radical,
and/or a vinyl compound of formula IV

**IV**

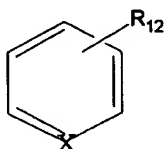
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wherein R_{10} is a straight or branched chain alkyl radical of from 1-4 carbons and R_{11} is given

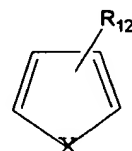
by formula V, VI or VII,



V

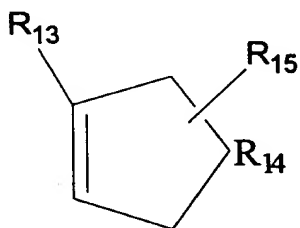


VI



VII

wherein R_{12} represents one or more alkyl radicals or one or more of H, Cl, OR and SO_3R_1 NO_2 , PO_3R_1 and X is a hetero atom other than carbon; and/or an olefin shown by formula VIII,



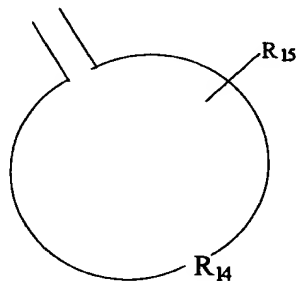
VIII

wherein R_{13} is Cl, or SO_3R_1 , alkyl, O-alkyl, O-aryl and R_{14} , represents from 4-20 carbon atoms such as to make H a cyclic or polycyclic alkane or polyalkenyl compound, R_{15} , is an

- 27 -

epoxide or SO_3R_1 reacted with an unsaturated portion of the ring comprising R_{14} ;

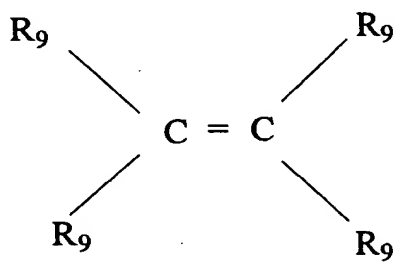
and/or an exocyclic olefin shown by formula IX



5

IX

and/or an internal olefin shown by formula X,



X

where R_9 is the same or different and as hereinabove defined.

The dispersant copolymers of the second embodiment of the present invention may also
5 include copolymers being the water soluble derivatives of a combination of an unsaturated
 α,β -unsaturated oxyacid or anhydride and another olefinic monomer, not limited to being of
an alternating structure, that may have been derivatised post copolymerisation such as to
provide the necessary substituents and enhance water solubility and regularity of charge or
polarity on the polymer. Such derivatisation includes that obtained from reaction of groups
10 pendant to the copolymer such as acids and acid derivatives with nucleophilic reagents such
as alcohols, amines and thiols to give esters, amides and thioesters respectively.

In a further form of derivatisation copolymers with residual reactive unsaturation may be
reacted with electrophilic or radical reagents such as peroxides or sulphite to give epoxides
15 and sulphonates respectively.

In a special case of the above, copolymers with pendant aryl or heteroaryl groups can be
made to undergo electrophilic aromatic substitution with sulphonating, nitrating and
phosphating reagents.

20

In a further form of derivatisation, copolymers with hydroxyl groups can be esterified with
acids including carboxylic, sulphuric and phosphoric acids.

The dispersants for use in the second embodiment of the present invention may advantageously be alternating copolymers as described hereinabove.

- 5 The copolymer may incorporate one or more first comonomers in addition to one or more of the second comonomers. The polymer may also contain additional comonomer residues. For example, the addition of a small amount, say less than 10%, of methyl methacrylate will not substantially change the character of the copolymer. The copolymer may contain residues of additional olefin comonomers. Suitable copolymers for use in the present
- 10 invention also include copolymers of three or more comonomers. Preferably, while not wishing to be bound by theory it appears that providing a consistent hydrophobic polymer backbone is provided in the presence of regularly spaced anionic charge or steric barrier along the polymer. The improved dispersant performance is preserved.
- 15 The preferred molecular weights of the copolymers of the second embodiment of the present invention are in the range of from 1000 to 90000 daltons. We have found that certain higher molecular weight copolymers show a certain degree of intractability in solution and our more preferred range is from 1000-30000 daltons, even more preferred is 1000-10000 daltons.
- 20 We have found that agriculturally acceptable salts of copolymers as described herein for use as dispersants in agricultural compositions provide improved and consistent dispersant performance when compared to conventionally used dispersants such as sulfonated

alkylnaphthalene formaldehyde condensate salts.

It is surprising that copolymers as described herein give enhanced performance when compared to previously described dispersants structures in the prior art such as for example
5 diisobutylene, isobutylene and styrene copolymers with maleic anhydride while still other derivatives described in those same publications, cannot be reasonably used as dispersants in agricultural applications at all. For example we have found that styrene-maleic anhydride copolymer derivatives resulted in an unstable dispersion. Similarly linear α -olefin maleic anhydride derivatives such as those derived from n-octene and n-decene also yielded unstable
10 dispersions affording poor suspensibility. However it was found that the substituted or derivatized copolymers of the above copolymers according to the second embodiment of the present invention showed improved performance.

The performance of the copolymers described herein has been observed at different dispersant
15 concentrations in WP and WG formulations to exhibit improved storage stability. Also we have found that in many cases it is possible to lower the dispersant concentration from normally accepted levels and retain an acceptable suspensibility result, thereby achieving more efficient the surface coverage of the dispersant. In practical terms this means the dispersant will be more cost effective to the end user. When the use rate of copolymers is compared
20 to that of a diisobutylene maleic anhydride sodium salt of similar molecular weight typically we have found that the copolymers of this invention may give acceptable stability at a concentration lower than the corresponding diisobutylene derivative. In addition the

formulations typically show improved dispersibility. When compared to sulfonated alkyl naphthalene formaldehyde condensates, suspensibility is significantly improved, even at lower concentrations.

- 5 Methods for making such copolymers of the second embodiment of the present invention from first and second comonomers will be well known to those skilled in the art of polymer synthesis. The comonomers of the present invention may be substituted prior to or post polymerization with methods which will be appreciated by those skilled in the art.
- 10 The dispersant system used in embodiments of the present invention may be a mixture of the copolymer as herein described with other dispersants known to those skilled in the art, including alkyl substituted and unsubstituted sulfonated naphthalene formaldehyde condensate salts, alkyl substituted and unsubstituted phenol formaldehyde condensate salts, lignosulphonate salts, polyacrylate salts, and previously described α -olefinic unsaturated
- 15 dicarboxylic acid copolymer derivatives.

In agrochemical applications, a wide variety of insoluble materials such as active principals are delivered in aqueous suspension. Active principals such as those used in WP, WG and SC formulations are generally insoluble at ambient temperatures. Water insoluble materials

20 which may advantageously be used in WP, WG and SC formulations include herbicides, insecticides, fungicides, biocides, molluscicides, algaicides, plant growth regulators, anthelmintics, rodenticides, nematocides, acaricides, amoebicides, protozoacide, crop safeners

and adjuvants. Examples of such actives commonly granulated or made as powders in agriculture include: triazine herbicides such as simazine, atrazine, terbutylazine, terbutryn and ametryn, urea herbicides such as diuron, sulphonyl urea herbicides such as chlorsulfuron, metsulfuron methyl, nicosulfuron and triasulfuron, sulphonanilide herbicides such as flumetsulam, organophosphate insecticides such as azinphos methyl, chlorpyrifos, sulprofos and azamethiphos, carbamate insecticides such as aldicarb, bendiocarb, carbaryl and BPMC, synthetic pyrethroids such as bifenthrin, as well as various types of fungicides including dimethomorph, benomyl, carbendazim, mancozeb, triazoles such as hexaconazole and diniconazole, acaricides such as propargite. A complete list of such products can be drawn from the Pesticide Dictionary (contained in the Farm Chemicals Handbook) or the British Crop Protection Society: Pesticides Manual.

In addition, some fertilizers and also water soluble active principles may use water dispersible formulations either by addition of inert carriers for convenience in handling or to aid in a controlled release formulation.

A wide variety of other insoluble materials are used in agricultural applications including fillers and carriers, for example but not limited to, natural and synthetic silicates and silicate minerals, mineral oxides and hydroxides and also natural and synthetically derived organic materials. Such materials may be added as porous carriers, as moisture inhibition agents, to aid binding or agglomeration properties of a formulation or simply to fill a formulation to a convenient weight. Examples of such fillers may include natural silicates such as

diatomaceous earth, synthetic precipitated silicas, clays such as kaolin, attapulgites and bentonites, zeolites, titanium dioxide, iron oxides and hydroxides, aluminium oxides and hydroxides, or organic materials such as bagasse, charcoal, or synthetic organic polymers. These other insoluble materials may be readily dispersed in accordance with the present invention.

An additional agent conventionally used in combination with dispersants used in the above formulations is a surfactant wetting agent. The role of the wetting agent in the case of SC formulations is to aid removal of air from particle surfaces during manufacture and to aid dilution in water. In the case of WP formulations the role of the wetter may be to aid penetration of the solids into water, while in the case of WG formulations it may aid penetration of the granules into water and aid disintegration of granules back to primary particle size. In some cases the dispersant may itself function as a suitable wetting agent while in others the dispersant may show an antagonistic effect on the wetter. As a further embodiment of the present invention at least one surfactant wetting agent may be selected from the group consisting of an alkylpolysaccharide; di or mono alkyl sulphosuccinate derivative; a nonionic surfactant loaded onto an inert silicate carrier; and a non-ionic surfactant delivered in the form of a urea surfactant complex.

The step of dispersing the formulation in an aqueous medium may be achieved by any convenient means dependent on the nature of the formulation. It is desirable that the dispersion of the formulation in an aqueous solution may be conducted either by hand or with

a minimum of mechanical agitation. Mechanical agitation may include stirring, mixing, blending and other similar processes.

The suspension of insoluble material in aqueous medium will be typically used for the treatment of a substrate such as plant or other agricultural medium. The application of the suspension onto the substrate may be achieved by any convenient means, including spraying, and the like. Granules are generally dispersed in water prior to being sprayed by the farmer. Farm sprays may be as a small back-pack handspray or a large boom spray or other convenient means. Aerial spraying is also sometimes used.

10

Formulations of the present invention may also be applied to the substrate directly, prior to dispersion. The subsequent application of rain or other aqueous media is sufficient for the formulation of the suspension of particulate material.

15 The present invention is described with reference to WP, WG and SC formulations. In each case, formulations provide a stable aqueous dispersion of finely milled insoluble hydrophobic particles. The stability properties of the dispersion and hence the effectiveness of the dispersion can be measured by means of a suspensibility test as described by the CIPAC test MT 15.1. In this test the volume fraction of suspended material is compared to that which has settled out due to gravity after 30 minutes. Typically a reported percentage suspensibility about 80% would be considered as an effective dispersant for WG and WP formulations, while in excess of 90% would be expected for an SC formulation. Another measure of the

stability of the dispersion is the degree to which particles remain non aggregated. This may also be a property of the even distribution of the dispersant in the formulation. The degree to which particles may be aggregated is often measured by a wet sieve retention test as described in CIPAC test MT 59.3. In this test the dispersed solid is poured through a series of fine sieves and retained material is measured as a fraction of the total amount of dispersed material. Formation of such aggregates is a major problem observed in WG formulations and to a lesser extent in WP formulations.

Generally WP formulations are produced by milling the active principle either in combination with fillers or alone to a suitable particle size, typically in the 5-15 μm range. The milled material is then dry blended, typically with a surfactant wetter, and dispersant to give a homogeneous composition. The powder formulation is assessed for wettability according to a method such as CIPAC MT 53.5.1 and suspensibility as per CIPAC MT 15.1. A formulation will desirably have a wettability of less than 1 minute and a suspensibility above 80%. Below 60% would generally be considered unacceptable. Results which might be commercially acceptable are either determined by the local registration authority or by the standards set by the formulators themselves.

In the case of WG formulations a suitably milled active ingredient with or without other fillers, typically of particle size 5 to 15 μm , is mixed with a surfactant wetter and dispersant. Typically an excess of water is added to bind the particles together into agglomerates. The excess water is later reduced by suitable air drying techniques to an optimal level.

The agglomerates are typically granulated using one of many techniques including pan granulation, drum granulation, fluid bed granulation, spray drying, tableting or extrusion techniques which are well known to those skilled in the art.

- 5 The wetter and dispersant may either be powder blended with the active ingredient or alternatively blended as an aqueous solution in the water used to aid agglomeration.

For a WG formulation to be acceptable an additional requirement is that the said granules should readily disperse in water back to the primary dispersed particle size within a short
10 period. This property is known as dispersibility and in describing the current invention it is measured as the time taken for granules to disperse back to primary particle size in water under a standard degree of agitation. A dispersion time of less than one minute is desirable, 20 seconds is excellent and 2 minutes is poor. Desirably the granules should also have good suspensibility. Suspensibility is typically tested using CIPAC MT 15.1. Above 80% is a
15 desirable result, less than 60% is generally regarded as undesirable. In many cases when testing granules a so-called maximum surface coverage result is often obtained. This is where the suspensibility results reach a maximum level then plateau. Adding more dispersant will not generally improve the result. This phenomenon is thought to be due to the particle size distribution of the material. Usually there is a given number of particles which are of such
20 a size that they will settle regardless of type and concentration of dispersant.

Desirably the granules should have low wet sieve retention. Wet sieve retention is typically

tested using CIPAC MT 59.3. For the 150 μm sieve less than 0.1% retained material is desirable. Less than 0.02% is more desirable. Likewise for the 53 μm sieve less than 0.6% is desirable, anything less than this is more desirable.

- 5 Storage stability may be tested by storage at 50 degrees celsius and tested as above at 1 month and 3 month intervals to determine if any properties have changed significantly.

Preferably, the granules should maintain these properties on storage. Surprisingly, it has been observed that, upon prolonged storage, solid formulations such as WP and WG formulations
10 containing dispersants such as those described herein are not as susceptible to deterioration in dispersability and suspensibility as formulations of the prior art.

We have also found that WP and WG formulations which incorporate the dispersants described herein require typically less dispersant, than for presently known WP and WG
15 formulations.

As a further embodiment of the present invention in the case of WP and WG formulations the dispersants herein described may be combined with surfactant wetting agents selected from the classes comprising alkylpolysaccharides, dialkyl and monoalkylsulphosuccinate salts,
20 nonionic surfactants loaded onto porous silicate carriers and urea surfactant complexes of non-ionic surfactants. The wetting agent may be combined in such formulations at a rate in excess of 1% w/w and preferably less than 3% w/w. Most preferred from the alkylpolysaccharide

class of wetting agents are alkylpolyglucosides derived from reaction with glucose and a primary hydrocarbon alcohol. Even more preferred are the highly crystalline derivatives such as obtained from ECOTERIC AS 20 and ECOTERIC AS10. Most preferred from the monoalkylsulphosuccinate class are sodium or potassium salts of cyclohexyl, iso-octyl and n-octyl sulphosuccinate. Most preferred from the dialkylsulphosuccinate class are sodium or potassium salts of dicyclohexyl, diisooctyl and di-n-octyl sulphosuccinates. Most preferred from the class of nonionic surfactants loaded onto insoluble porous silicate carriers are ethoxylated surfactants loaded onto carriers such as TERIC 157. Most preferred wetting agents from the urea surfactant complexes are urea adducts of alcohol ethoxylate surfactants such as ATPLUS G73050. The wetters herein described show good wettability and dispersibility for the formulations and have the additional advantage of showing storage stability in combination with the copolymer dispersants described. Whereas by comparison some commonly used WG and WP wetters such as alkyl naphthalene sulphonate salts and lignosulphonate salts have been found to show poor storage stability.

15

In the case of SC formulations in the present invention an active ingredient is typically added to water containing a dispersant, preferably with a surfactant wetting agent together with a conventional non-ionic dispersant. A humectant may also be included. A dispersion is formed using high shear mixing. The dispersion is then milled by any one of several means of wet milling so that the mean particle size of the dispersed solid is below 5 μm more typically in the range of from 1 to 3 μm . The resulting product is known as a millbase and may be modified with additives such as antifreeze, thickeners and antisetling agents, biocides

and colouring agents may be added. For an SC formulation to be acceptable it should not show a high degree of thickening, settling or growth of aggregates over time. These physical properties can be assessed by visual observation.

- 5 SC's generally require good viscosity and storage stability. Storage stability is usually assessed as degree of top settling or syneresis, sedimenting or "claying" which is the tendency to form a sticky layer on the bottom and "bleeding" which is the tendency of the dispersion to separate without necessarily displaying even settling. Redispersibility is also important. These may also be assessed visually.

10

- For SC formulations in the case of dispersants described herein only certain dispersant copolymers are suitable. When used alone, some dispersant copolymer derivatives give a viscosity of slurry premix unsuitable for milling so it is preferable to combine the dispersant with another fast acting well known dispersant such as an EO/PO block co-polymer type
- 15 dispersant. While not wishing to be bound by theory it appears that the dispersant needs time to migrate to the surface of the dispersed particles. The dispersant copolymers are used synergistically with other known dispersants in some cases.

- While the present invention has been described with reference to agrochemical formulations,
- 20 it will be apparent that the improvements in dispersibility and suspensibility will render the present invention useful in other applications. The present invention will now be further described with reference to the following non-limiting examples and figures. All percentages

recited herein are by weight of the total composition unless otherwise specified.

Example 1.

A Simazine 900g/kg WG formulation of the following composition was prepared.

| | | |
|---|---------------------------|------------|
| 5 | Simazine tech. (98 % w/w) | 91.8 % w/w |
| | MORWET EFW | 1.5 |
| | DISPERSANT | 6.2 |
| | Water | 0.5% |

The dispersant used was an alkylnaphthalene formaldehyde condensate salt, SCS 2258.

- 10 The granules were prepared by blending the solids with approximately 15% by weight of water such as to give a plastic premix which was then extruded using a Fuji-Paudal laboratory scale extrusion granulator. The resulting granules were then dried by means of a fluid bed drier back to a water content of approximately 0.5% w/w.

- 15 The resulting WG was tested for dispersibility by recording the time in seconds required for total disintegration under uniform agitation. The suspensibility was tested according to CIPAC MT 15.1 and the wet sieve retention was tested using 150 micron and 53 micron sieves according to CIPAC MT 59.3. Results are recorded in TABLE 1.

Example 2

A simazine 900 g/Kg WG was prepared and tested as described in example 1 where the dispersant used was POLYFON H, a lignosulphonate salt. The results are described in TABLE 1.

5

Example 3.

A Simazine 900g/kg WG formulation of the following composition was prepared :

| | | |
|----|---------------------------|------------|
| | Simazine tech. (98 % w/w) | 91.8 % w/w |
| | ATPLUS G73050 | 1.5 |
| 10 | DISPERSANT | 3.1 |
| | Kaolin | 3.1 |
| | Water | 0.5% |

The dispersant used was the sodium salt of an alternating copolymer of n-octene and maleic anhydride of approximate molecular weight 13000. The granules were prepared and tested

15 in the manner described in Example 1. The results are shown in TABLE 1.

Example 4.

A Simazine 900g/kg WG formulation was prepared and tested in the manner described in Example 3 with the dispersant being the sodium salt of a co-polymer of n-decene and maleic

20 anhydride. Results are shown in TABLE 1.

Example 5.

A Simazine 900g/kg WG formulation was prepared and tested in the manner described in Example 3 with the dispersant being the sodium salt of a co-polymer of diisobutylene and maleic anhydride of approximate molecular weight 16000. Results are shown in TABLE 1.

5

Example 6.

A WG formulation was prepared and tested as described in Example 3 with the dispersant being the sodium salt of an alternating copolymer of styrene and maleic anhydride. Results are shown in TABLE 1.

10

Example 7.

A WG formulation was prepared and tested as described in Example 3 with the dispersant being the sodium salt of SMA 3000 which is a 3:1 copolymer of styrene and maleic anhydride. Results are shown in TABLE 1.

15

Example 8.

A WG formulation was prepared and tested as described in Example 3 with the dispersant being the sodium salt of GANTREZ AN 119 resin which is a copolymer of methylvinyl ether and maleic anhydride. Results are shown in TABLE 1.

20

Example 9.

A Simazine 900g/kg WG formulation of the following composition was prepared.

| | | |
|---|---------------------------|------------|
| | Simazine tech. (98 % w/w) | 91.8 % w/w |
| | ATPLUS G73050 | 1.5 |
| 5 | DISPERSANT | 6.2 |
| | Water | 0.5 % |

The dispersant used was the monoammonium salt of an alternating copolymer of diisobutylene and maleic anhydride. The granules were prepared and tested in the manner described in Example 1. Results are shown in TABLE 1.

10

Example 10

A Simazine 900g/kg WG formulation of the following composition was prepared :

| | | |
|----|---------------------------|------------|
| | Simazine tech. (98 % w/w) | 91.8 % w/w |
| | ATPLUS G73050 | 1.5 |
| 15 | DISPERSANT | 3.1 |
| | Kaolin | 3.1 |
| | Water | 0.5 % |

The dispersant used was the sodium salt of an alternating copolymer of undecylenic acid and maleic anhydride. The granules were prepared and tested in the manner described in
20 example1. Results are shown in TABLE 2.

Example 11

~~A Simazine 900g/kg WG formulation was prepared and tested in the manner described in~~

Example 10 with the dispersant being the sodium salt of an alternating co-polymer of vinyl isobutyl ether and maleic anhydride. Results are shown in TABLE 2.

5

Example 12

A Simazine 900g/kg WG formulation was prepared and tested in the manner described in Example 10 with the dispersant being the sodium salt of an alternating co-polymer of alphas-methyl styrene and maleic anhydride. Results are shown in TABLE 2.

10

Example 13

A Simazine 900g/kg WG formulation was prepared and tested in the manner described in Example 10 with the dispersant being the sodium salt of a non-alternating co-polymer of alphas-methyl styrene and maleic anhydride. Results are shown in TABLE 2.

15

Example 14

A Simazine 900g/kg WG formulation was prepared and tested in the manner described in Example 10 with the dispersant being the benzyltrimethylammonium salt of an alternating co-polymer of alphas-methyl styrene and maleic anhydride. Results are shown in TABLE 2.

20

Example 15

A Simazine 900g/kg WG formulation was prepared and tested in the manner described in Example 10 with the dispersant being the sodium salt of an alternating co-polymer of d-limonene and maleic anhydride. Results are shown in TABLE 2.

5

Example 16

A Simazine 900g/kg WG formulation was prepared and tested in the manner described in Example 10 with the dispersant being the sodium salt of an alternating co-polymer of β -pinene and maleic anhydride. Results are shown in TABLE 2.

10

Example 17

A Simazine 900g/kg WG formulation was prepared and tested in the manner described in Example 10 with the dispersant being the sodium salt of an alternating co-polymer of dimethyldicyclopentadiene and maleic anhydride. Results are shown in TABLE 2.

15

Example 18

A Simazine 900g/kg WG formulation was prepared and tested in the manner described in Example 10 with the dispersant being the sodium salt of an alternating co-polymer of dicyclopentadiene and maleic anhydride. Results are shown in TABLE 2.

20

Example 19

An Atrazine 900g/kg WG formulation of the following composition was prepared.

| | | |
|---|--------------------------|------------|
| | Atrazine tech. (98% w/w) | 91.8 % w/w |
| | ATPLUS G73050 | 1.5 |
| 5 | DISPERSANT | 3.1 |
| | Kaolin | 3.1 |
| | Water | 0.5 |

where the dispersant used was the sodium salt of an alternating copolymer of dicyclopentadiene and maleic anhydride. The granules were made and tested as described in

10 Example 1. Results are shown in TABLE 2.

Example 20

An Atrazine 900g/kg WG formulation was prepared and tested in the manner described in Example 19 with the dispersant being the sodium salt of an alternating co-polymer of

15 alphanemethylstyrene and maleic anhydride. Results are shown in TABLE 2.

Example 21

A Diuron 900g/kg WG formulation of the following composition was prepared.

| | | |
|---|------------------------|------------|
| | Diuron tech. (97% w/w) | 92.8 % w/w |
| | ATPLUS G73050 | 1.5 |
| 5 | DISPERSANT | 3.1 |
| | Kaolin | 2.1 |
| | Water | 0.5 |

where the dispersant used was the sodium salt of an alternating copolymer of dicyclopentadiene and maleic anhydride. The granules were made and tested as described in
10 example 1. Results are shown in TABLE 2.

Example 22

A Diuron 900g/kg WG formulation was prepared and tested in the manner described in example 21 with the dispersant being the sodium salt of an alternating co-polymer of
15 alphas-methylstyrene and maleic anhydride. Results are shown in TABLE 2.

Example 23

A Simazine 900g/kg WG formulation of the following composition was prepared :

| | | |
|---|---------------------------|------------|
| | Simazine tech. (98 % w/w) | 91.8 % w/w |
| | ATPLUS G73050 | 1.5 |
| 5 | DISPERSANT | 3.1 |
| | Kaolin | 3.1 |
| | Water | 0.5 % |

The dispersant used was the sodium salt of a copolymer of n-octene and maleic anhydride derivatised by reaction with morpholine to give a morpholine amide derivative. The granules
10 were prepared and tested in the manner described in Example 1. Results are shown in TABLE 3.

Example 24

A Simazine 900g/kg WG formulation was prepared and tested in the manner described in
15 Example 23 with the dispersant being the sodium salt of the morpholine amide derivative of a co-polymer of n-decene and maleic anhydride. Results are shown in TABLE 3.

Example 25

A Simazine 900g/kg WG formulation was prepared and tested in the manner described in
20 example 23 with the dispersant being the sodium salt of the morpholine amide derivative of SMA 1000, a 1:1 co-polymer of styrene and maleic anhydride. Results are shown in TABLE 3.

Example 26

A Simazine 900g/kg WG formulation was prepared and tested in the manner described in

Example 23 with the dispersant being the sodium salt of the morpholine amide derivative of SMA 3000, a 3:1 co-polymer of styrene and maleic anhydride. Results are shown in TABLE

5 3.

Example 27

A Simazine 900g/kg WG formulation was prepared and tested in the manner described in Example 23 with the dispersant being the sodium salt of the aromatic sulphonated derivative of SMA 1000, a 1:1 co-polymer of styrene and maleic anhydride. Results are shown in TABLE 3.

Example 28

A Simazine 900g/kg WG formulation was prepared and tested in the manner described in Example 23 with the dispersant being the sodium salt of the morpholine amide derivative of Gantrez AN119, a co-polymer of methylvinyl ether and maleic anhydride. Results are shown in TABLE 3.

Example 29

A Simazine 900g/kg WG formulation was prepared and tested in the manner described in Example 23 with the dispersant being the sodium salt of the co-polymer of alphas-methylstyrene and maleic anhydride derivatised with ammonia to give the corresponding monoamide. Results are shown in TABLE 3.

Example 30

~~A Simazine 900g/kg WG formulation was prepared and tested in the manner described in~~

Example 23 with the dispersant being the monoammonium salt of the co-polymer of
alphamethylstyrene and maleic anhydride derivatised with ammonia to give the corresponding
5 monoamide. Results are shown in TABLE 3.

Example 31

A Simazine 900g/kg WG formulation was prepared and tested in the manner described in
Example 23 with the dispersant being the sodium salt of the co-polymer of alphamethylstyrene
10 and maleic anhydride derivatised with ethanolamine to give the corresponding ethanolamide.
Results are shown in TABLE 3.

Example 32

A Simazine 900g/kg WG formulation was prepared and tested in the manner described in
15 Example 23 with the dispersant being the sodium salt of the co-polymer of alphamethylstyrene
and maleic anhydride derivatised with n-butylamine to give the corresponding n-butylamide.
Results are shown in TABLE 3.

Example 33

20 A Simazine 900g/kg WG formulation was prepared and tested in the manner described in
Example 23 with the dispersant being the sodium salt of the co-polymer of alphamethylstyrene
and maleic anhydride derivatised with morpholine to give the corresponding morpholine

amide. Results are shown in Table 3.

Example 34

- A Simazine 900g/kg WG formulation was prepared and tested in the manner described in Example 23 with the dispersant being the sodium salt of the co-polymer of dicyclopentadiene and maleic anhydride derivatised morpholine to give the corresponding amide. Results are shown in TABLE 3.

Example 35

- 10 A Simazine 900g/kg WG formulation was prepared and tested in the manner described in Example 23 with the dispersant being a sulphonated derivative of the sodium salt of the co-polymer of dicyclopentadiene and maleic anhydride. Results are shown in TABLE 3.

Example 36

- 15 A Simazine 900g/kg WG formulation was prepared and tested in the manner described in Example 23 with the dispersant being the sodium salt of the co-polymer of dimethyldicyclopentadiene and maleic anhydride derivatised with morpholine to give the corresponding morpholine amide. Results are shown in TABLE 3.

20 Example 37

- A Simazine 900g/kg WG formulation was prepared and tested in the manner described in Example 23 with the dispersant being a sulphonated derivative of the sodium salt of the co-

polymer of dimethyldicyclopentadiene and maleic anhydride. Results are shown in TABLE

3.

Example 38

5 A Simazine 900g/kg WP formulation of the following composition was prepared by blending the following :

| | | |
|----|---------------------------|------------|
| | Simazine tech. (98 % w/w) | 91.8 % w/w |
| | ATPLUS G 73050 | 1.7 |
| | DISPERSANT | 3.1 |
| 10 | Kaolin | 3.4 |

where the dispersant used was the sodium salt an alternating copolymer of dicyclopentadiene and maleic anhydride. Results are shown in TABLE 4. The wettability of the WP was also measured according to CIPAC test MT 53.5.1.

15 Example 39

A Simazine 900g/kg WP formulation of the following composition was prepared and tested in the manner described in example 38 where the dispersant used was the sodium salt an alternating copolymer of dicyclopentadiene and maleic anhydride used at 3.1% w/w, the wetting agent was the sodium salt dicyclohexylsulphosuccinate used at 1.7% w/w. Results
20 are shown in TABLE 4.

Example 40

A Simazine 900 g/Kg WP formulation was prepared and tested as described in example 38

excepting that the wetting agent used was ECOTERIC AS 20, an alkylpolysaccharide used at 1.7% w/w on an active basis (the product is a 50% solution in water). The results are shown in TABLE 4.

5 Example 41

A Simazine 900 g/Kg WP formulation was prepared and tested as described in example 38 excepting that the wetting agent used was TERIC 157 a nonionic wetter loaded onto an insoluble porous carrier used at 1.7% w/w. The results are shown in TABLE 4.

10 Example 42

A Simazine 900g/kg WG formulation of the following composition was prepared :

| | |
|--------------------------|------------|
| Simazine tech. (98% w/w) | 91.8 % w/w |
| WETTER | 1.5 |
| DISPERSANT | 6.2 |
| 15 Water | 0.5% |

The dispersant used was the sodium salt of an alternating copolymer of alphas-methylstyrene and maleic anhydride of approximate molecular weight 16000 and the wetter used was MORWET EFW a sulphonated naphthalene derivative salt. The granules were prepared and tested in the manner described in Example 1. The results are shown in TABLE 5.

Example 43

~~A Simazine 900g/Kg WG formulation was prepared and tested in the manner described in~~
 example 42. The dispersant used was the sodium salt of an alternating copolymer of
 alphamethylstyrene and maleic anhydride and the wetter used was the sodium salt of
 5 dicyclohexylsulphosuccinate. The results are shown in TABLE 5.

Example 44

An Atrazine 900g/Kg SC formulation of the following composition was prepared.

| | | |
|----|------------------------|------------|
| | Atrazine tech. 97% w/w | 51.5 % w/v |
| 10 | Monoethylene glycol | 4.0 |
| | ATLOX 4896A | 3 |
| | DISPERSANT | 2 |
| | Silicone antifoam | 0.2 |
| | Rhodopol 23 | 0.2 |
| 15 | Proxel GXL 20 | 0.1 |
| | Water. | 55.0 |

The dispersant used was the sodium salt of an alternating copolymer of alphamethylstyrene
 and maleic anhydride. The SC was prepared by dissolving the monoethylene glycol,
 20 ATLOX 4896A and DISPERSANT in 85% of the water and adding the Atrazine tech. and
 antifoam with vigorous mixing to form a slurry or millbase premix. The premix is then
 milled using a Dynomill laboratory scale bead mill to give a suitable particle size distribution

of > 98% of particles below 5 microns. The millbase thus obtained was then blended with

~~Proxel GXL 20 and Rodopol 23 in a premix and then made up to the desired volume with~~

the remaining water and mixed to a homogeneous mixture. The SC thus obtained was of usable viscosity and was found to be storage stable after storage at 2 degrees C and 50 degrees C for one month, with minimal syneresis and thickening and no claying, sedimentation or aggregates being observed.

Example 45

It was attempted to make an SC formulation according to the formula and method of example 44 with 4% w/w of the sodium salt of an alternating copolymer of alphas-methylstyrene and maleic anhydride and only 1% w/w ATLOX 4896A being used. the resulting millbase premix was of a viscosity which would not allow it to be milled.

Example 46

15 An Atrazine 900g/Kg SC formulation of the following composition was prepared.

| | |
|------------------------|------------|
| Atrazine tech. 97% w/w | 51.5 % w/v |
| Monoethylene glycol | 4.0 |
| DISPERSANT | 4 |
| Silicone antifoam | 0.2 |
| Rhodopol 23 | 0.2 |
| Proxel GXL 20 | 0.1 |
| Water. | 55.0 |

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The dispersant used was the sodium salt of a sulphonated copolymer of dicyclopentadiene and

maleic anhydride. The SC was prepared in the manner described in example 44. The SC

thus obtained was of usable viscosity and was found to be storage stable after storage at 2 degrees C and 50 degrees C for one month, with minimal syneresis and thickening and no
5 claying, sedimentation or aggregates being observed.

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TABLE 1
WDG Results from Prior Art

| Exempl e No. | Dispersibility (Seconds) | | | Suspensibility (%) | | | Wet Sieve Retention (%) | | | | | |
|-----------------|-----------------------------|----------------|----------------|-----------------------|----------------|----------------|-------------------------|----------------|----------------|----------------|----------------|----------------|
| | T ₀ | T ₁ | T ₃ | T ₀ | T ₁ | T ₃ | T ₀ | T ₁ | T ₃ | T ₀ | T ₁ | T ₃ |
| 1 | 52 | 46 | 44 | 82 | 63 | 69 | 0.087 | 0.41 | 2.2 | 0.033 | 1.53 | 1.70 |
| 2 | 58 | 45 | 46 | 80 | 68 | 70 | 0.029 | 1.09 | 0.92 | 0.486 | 4.10 | 4.70 |
| 3 | 36 | - | - | 39 | - | - | - | - | - | - | - | - |
| 4 | 33 | - | - | 59 | - | - | 0.002 | - | - | 0.042 | - | - |
| 5 | 60 | 54 | 50 | 72 | 78 | 71 | 0.02 | 0.02 | 0.016 | 0.15 | 0.21 | 0.28 |
| 6 | 55 | - | - | 31 | - | - | 0.027 | - | - | 0.095 | - | - |
| 7 | >280 | - | - | <10 | - | - | - | - | - | - | - | - |
| 8 | 53 | - | - | 48 | - | - | 0.002 | - | - | 0.085 | - | - |
| 9 | >200 | - | - | <10 | - | - | - | - | - | - | - | - |

T₀ initial results
T₁ after 1 month storage at 50°C
T₃ after 3 months storage at 50°C

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TABLE 2
WG Formulation of First Embodiment

| Example No. | Dispersibility | | | Suspensibility | | | Wet Sieve Retention (%) | | | | | |
|-------------|----------------|----------------|----------------|----------------|----------------|----------------|-------------------------|----------------|----------------|----------------|----------------|----------------|
| | T ₀ | T ₁ | T ₃ | T ₀ | T ₁ | T ₃ | T ₀ | T ₁ | T ₃ | T ₀ | T ₁ | T ₃ |
| 10 | 65 | 54 | - | 79 | 48 | - | 0.004 | 0.007 | - | 0.044 | 0.053 | - |
| 11 | 67 | 68 | 62 | 84 | 83 | 84 | 0.002 | 0.007 | 0.001 | 0.052 | 0.073 | 0.079 |
| 12 | 78 | 70 | 72 | 83 | 86 | 85 | 0.020 | 0.010 | 0.010 | 0.080 | 0.09 | 0.096 |
| 13 | 119 | - | - | 86 | - | - | 0.167 | - | - | 0.651 | - | - |
| 14 | 68 | >180 | - | 83 | 66 | - | 0.014 | 1.04 | - | 0.119 | 5.81 | - |
| 15 | 60 | 72 | 54 | 86 | 83 | 84 | 0.001 | 0.008 | 0.009 | 0.060 | 0.05 | 0.05 |
| 16 | 55 | 40 | 50 | 85 | 85 | 84 | 0.005 | 0.009 | 0.003 | 0.051 | 0.058 | 0.058 |
| 17 | 29 | 32 | 28 | 86 | 86 | 87 | 0.012 | 0.005 | 0.005 | 0.044 | 0.048 | 0.051 |
| 18 | 40 | 43 | 56 | 85 | 87 | 88 | 0.010 | 0.002 | 0.007 | 0.060 | 0.048 | 0.084 |
| 19 | 56 | 50 | * | 86 | 86 | * | 0.014 | - | * | 0.38 | | * |
| 20 | 30 | 45 | * | 88 | 86 | * | 0.090 | 0.031 | * | 0.60 | 0.67 | * |
| 21 | 37 | 40 | * | 78 | 76 | * | 0.005 | 0.001 | * | 0.055 | 0.01 | * |
| 22 | 40 | 45 | * | 62 | 68 | * | 0.009 | 0.001 | * | 0.581 | 0.55 | * |

20 T₀ initial resultsT₁ after 1 month storage at 50°CT₃ after 3 months storage at 50°C

* Data not yet available

- Testing discontinued

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TABLE 3
WG Formulations using Dispersants of Second Embodiment

| Example No. | Dispersibility | | Suspensibility | | Wet Sieve Retention (%) | | | |
|-------------|----------------|----------------|----------------|----------------|-------------------------|----------------|----------------|----------------|
| | T ₀ | T ₁ | T ₀ | T ₁ | T ₀ | T ₁ | T ₀ | T ₁ |
| 23 | 71 | 45 | 87 | 82 | 0.10 | 0.10 | 0.068 | 0.21 |
| 24 | 95 | 85 | 75 | 68 | 0.005 | 0.001 | 0.042 | 0.051 |
| 25 | 67 | 62 | 85 | 83 | 0.005 | 0.002 | 0.060 | 0.118 |
| 26 | 28 | 26 | 84 | 88 | 0.001 | 0.005 | 0.039 | 0.052 |
| 27 | 58 | 56 | 85 | 83 | 0.038 | 0.068 | 0.195 | 0.140 |
| 28 | 57 | 36 | 87 | 72 | 0.002 | 0.55 | 0.061 | 5.64 |
| 29 | 68 | 68 | 83 | 83 | 0.001 | 0.004 | 0.051 | 0.054 |
| 30 | >180 | - | 6 | - | - | - | - | - |
| 31 | 10 | - | 70 | - | 0.05 | - | 2.79 | - |
| 32 | 68 | 40 | 81 | 77 | 0.005 | 0.012 | 0.044 | 0.092 |
| 33 | 53 | * | 86 | * | 0.005 | * | 0.065 | * |
| 34 | 40 | 32 | 87 | 85 | 0.004 | 0.007 | 0.051 | 0.313 |
| 35 | 26 | 33 | 86 | 86 | 0.001 | 0.001 | 0.045 | 0.053 |
| 36 | 57 | 44 | 85 | 86 | 0.002 | 0.008 | 0.064 | 0.199 |
| 37 | 32 | 30 | 87 | 87 | 0.001 | 0.005 | 0.054 | 0.048 |

* Data not yet available
- Testing discontinued

T₀ initial results
T₁ after 1 month storage at 50°C

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TABLE 4

WP Test Results

Simazine 900g/kg with various wetters

| Example No | Static Wetting Time (Seconds) | Suspensibility (%) |
|------------|----------------------------------|-----------------------|
| 38 | 79 | 78 |
| 39 | 67 | 78 |
| 40 | 68 | 79 |
| 41 | 60 | 79 |

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TABLE 5

WG Test Results

Simazine 900g/kg with various wetters

| Example No. | Dispersibility (seconds) | | Suspensibility (%) | | Wet Sieve Retention (%) | | | |
|----------------|-----------------------------|----------------|-----------------------|----------------|-------------------------|----------------|----------------|----------------|
| | T ₀ | T ₁ | T ₀ | T ₁ | T ₀ | T ₁ | T ₀ | T ₁ |
| 42 | 50 | 41 | 84 | 68 | 0.015 | 0.081 | 0.033 | 4.1 |
| 43 | 68 | 56 | 88 | 87 | 0.065 | 0.025 | 0.15 | 0.089 |

~~Those skilled in the art will appreciate that the invention described herein is susceptible to~~

variations and modifications other than those specifically described. It is to be understood that the invention includes all such variations and modifications which fall within its spirit
5 and scope. The invention also includes all of the steps, features, compositions and compounds referred to or indicated in this specification, individually or collectively, and any and all combinations of any two or more of said steps or features.

DATED this 13th day of October, 1997.

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By its Patent Attorneys

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